

e. The saturated liquid properties were obtained by subtracting the entropy and enthalpy changes due to vaporization from the saturated vapor value.

f. The saturated liquid line, as calculated in step e, was then used as the datum point for calculating properties below the critical temperature and densities greater than those of the saturated liquid. These properties were calculated by the isothermal integration of the appropriate portions of eqs (49) and (50). These expressions are

$$S = S^l - \int_{\tau}^{\rho} \left[ \frac{1}{\rho^2} \left( \frac{\partial P}{\partial T} \right)_{\rho} \right] d\rho$$

and

$$H = H^l + \frac{P}{\rho} - \frac{P}{\rho^l} + \int_{\tau}^{\rho} \left[ \frac{P}{\rho^2} - \frac{T}{\rho^2} \left( \frac{\partial P}{\partial T} \right)_{\rho} \right] d\rho$$

By progressing through the above procedure, the derived properties were calculated for the entire portion of the thermodynamic surface under consideration. However, the method of calculation outlined above may result in a discontinuity. This discontinuity exists at temperatures below the critical temperature for pressures above the critical pressure. The cause of the discontinuity arises from the fact that the calculation of the derived properties was performed by one procedure for temperatures above the critical temperature and a second procedure for temperatures below the critical. For temperatures below the critical, the changes of entropy and enthalpy due to vaporization had to be calculated as outlined in step d, and the saturated liquid line obtained as outlined in step e. For temperatures above the critical, steps d and e were not needed for the calculation of derived properties. The mutual boundary (at the critical temperature) between these two regions then exhibited the discontinuity. This discontinuity in the derived properties is possibly due to slight disagreement between the isochoric slope of the equation of state (40) at the critical point and the slope of the independently obtained vapor pressure equation (14) at the same point.

When the discontinuities were plotted with a highly expanded scale, it was determined that the discontinuity was independent of pressure. Adjustments to the derived properties were then determined by smoothing the transition region for isobars near the critical. These adjustments were applied to the derived properties by making appropriate corrections to the entropy and enthalpy of vaporization. The adjustments were added to the entropy and enthalpy of vaporization, thus decreasing the values for the entropy and enthalpy of the saturated liquid. Table 10 lists the temperature dependent adjustments which were made.

All of the data which have been calculated were restricted to the liquid and gaseous regions by using

TABLE 10. Adjustments for entropy and enthalpy of the saturated liquid

Temperature K	Entropy J/g - K adjustment <sup>a</sup>	Enthalpy J/g adjustment <sup>a</sup>
150	0.009539	1.431
149	.009750	1.453
148	.008768	1.298
147	.007549	1.110
146	.006330	0.924
145	.005189	.752
144	.004160	.599
143	.003249	.465
142	.002460	.349
141	.001789	.252
140	.001239	.173
139	.000811	.113
138	.000490	.068
137	.000260	.036
136	.000100	.014
135	.000010	.001

<sup>a</sup> These adjustments have been subtracted from the entropy and enthalpy of the saturated liquid.

the following melting curve relationship:

$$P_{\text{melt}} = P_t + A \left[ \left( \frac{T_{\text{melt}}}{T_t} \right)^C - 1 \right]. \quad (54)$$

In eq (54),  $A$  and  $C$  are constants which were determined by a least squares fit to experimental data. The form of this melting curve relationship is discussed by Goodwin and Weber [32].

The experimental data which were considered for the determination of the constant in eq (54) were taken from Michels and Prins [33], Lahr and Eversole [34], and Bridgman [35]. The constants of eq (54) were determined to be

$$A = 2078.76667$$

$$C = 1.59817868,$$

with a mean of the absolute pressure deviations of 0.08 percent.

The properties, density, enthalpy, internal energy, and entropy, are presented as functions of pressure and temperature in the tables of appendix A. The number of significant figures given in these tables is not justified on the basis of the uncertainties of the data, but, rather, is desirable to maintain the internal consistency of the tables.

A comparison of the heat of vaporization was made at the normal boiling point. The heat of vaporization of various investigators was compared with the value obtained by using the equation of state (40) and vapor pressure equation (14). This comparison is shown in table 11.

TABLE 11. Comparison of heat of vaporization at the normal boiling point

Frank and Clusius [36] .....	1557.5 ± 1.5	cal/g-mol
Flubacher et al. [15] .....	1555.0 ± 4.6	cal/g-mol
Eucken [37] .....	1501	cal/g-mol
Ziegler et al. [2] .....	1543.4	cal/g-mol
This work .....	1546.3	cal/g-mol

## 11. Equation of State and Saturation Boundary

The saturation boundary can be defined by the equation of state if there is a sufficient number of highly precise experimental  $P$ - $V$ - $T$  data points along the entire boundary. However, saturation densities are difficult to measure with high precision. In addition, for argon there was only one source of satisfactory saturation data, and these data did not cover the entire two-phase boundary. Therefore, it was difficult to perform a critical evaluation of these saturation data for the purpose of determining the saturation boundary.

Instead, there was available a relatively large number of  $P$ - $T$  data points along the saturation boundary. For these data, the vapor pressure equation (14) was developed. Therefore, the definition of the saturation boundary was obtained by the use of two independent equations—the equation of state (40) and the vapor pressure equation (14).

The saturation boundary, as defined by the equation of state alone, was then examined for internal thermodynamic consistency by using the conditions of thermodynamic equilibrium:

$$\begin{aligned} T^l &= T^g \\ P^l &= P^g \\ G^l &= G^g \end{aligned} \quad (55)$$

The equation of state (40) is a continuous function with a van der Waals form across the saturation boundary. Therefore, the equation for thermodynamic equilibrium (55) could be substituted into the equation of state (40). This was accomplished for a given saturation temperature by imposing the equilibrium conditions upon both the equation

of state and the equation for the Gibbs function derived from the equation of state and solving them iteratively and simultaneously for the corresponding density. By this means the entire saturation boundary was derived by the use of the equation of state and the conditions of thermodynamic equilibrium, without using the independently obtained vapor pressure equation (14).

A comparison of the vapor pressures as derived from the equation of state and the vapor pressures as obtained from the vapor pressure equation was made. The results of this comparison are shown in table 12 for 5-deg temperature increments.

The agreement shown in table 12 indicates that the equation of state is internally consistent with the conditions of thermodynamic equilibrium. Table 12 also indicates that the equation of state satisfactorily predicts  $P$ - $V$ - $T$  values in the vicinity of the saturation boundary.

TABLE 12. Vapor pressure comparison

$T, K$	$P_1, \text{Atm}$	$P_2, \text{Atm}$	$P_1 - P_2$
85	0.77945	0.79737	-0.01792
90	1.32133	1.34210	-0.02077
95	2.11103	2.13029	-0.01926
100	3.20974	3.22249	-0.01275
105	4.68121	4.68277	-0.00156
110	6.59102	6.57784	0.01318
115	9.00650	8.97649	0.03001
120	11.99740	11.94960	0.04780
125	15.63733	15.57082	0.06651
130	20.00587	19.91829	0.08758
135	25.19168	25.07827	0.11341
140	31.29662	31.15296	0.14366
145	38.44154	38.28020	0.16134
150	46.77419	46.71197	0.06222

$P_1$  is calculated from vapor pressure equation (14).  
 $P_2$  is calculated from equation of state (40).

## 12. Second Virial Coefficient and Intermolecular Potential

An equation of state which has been extensively used is

$$\frac{PV}{RT} = Z = 1 + B\rho + C\rho^2 + D\rho^3 + \dots, \quad (56)$$

where  $B, C, D, \dots$  are virial coefficients and represent deviations from ideal gas behavior. The virial coefficients are functions of temperature and are related to interactions between molecules. The second virial coefficient,  $B$ , is related to interactions between two molecules, the third virial,  $C$ , to the interaction between three molecules, etc. When the gas has negligible molecular interaction as compared to interaction with the walls of the confining vessel, then eq (56) reduces to the perfect gas where  $Z=1$ .

The virial coefficients for the equation of state (40) were obtained by arranging the equation of state into virial form as shown in eq (56). In order to obtain the proper form, the exponential term of eq (40) was expanded as

$$\begin{aligned} \exp(-n_{16}\rho^2) &= 1 - (n_{16}\rho^2) + \frac{(n_{16}\rho^2)^2}{2!} \\ &\quad - \frac{(n_{16}\rho^2)^3}{3!} + \dots \end{aligned} \quad (57)$$

Substituting eq (57) into eq (40),

$$\begin{aligned} Z &= 1 + \rho \left( \frac{n_1}{R} + \frac{n_2}{RT} + \frac{n_3}{RT^2} + \frac{n_4}{RT^3} + \frac{n_5}{RT^5} \right) \\ &\quad + \rho^2 \left( \frac{n_6}{R} + \frac{n_7}{RT} + \frac{n_9}{RT^3} + \frac{n_{10}}{RT^4} + \frac{n_{11}}{RT^5} \right) + \rho^3 \left( \frac{n_8}{R} \right) \\ &\quad + \rho^4 \left( \frac{n_{12}}{RT^3} + \frac{n_{13}}{RT^4} + \frac{n_{14}}{RT^5} - \frac{n_{16}n_9}{RT^3} \right. \\ &\quad \left. - \frac{n_{16}n_{10}}{RT^4} - \frac{n_{16}n_{11}}{RT^5} \right) + \dots \end{aligned} \quad (58)$$